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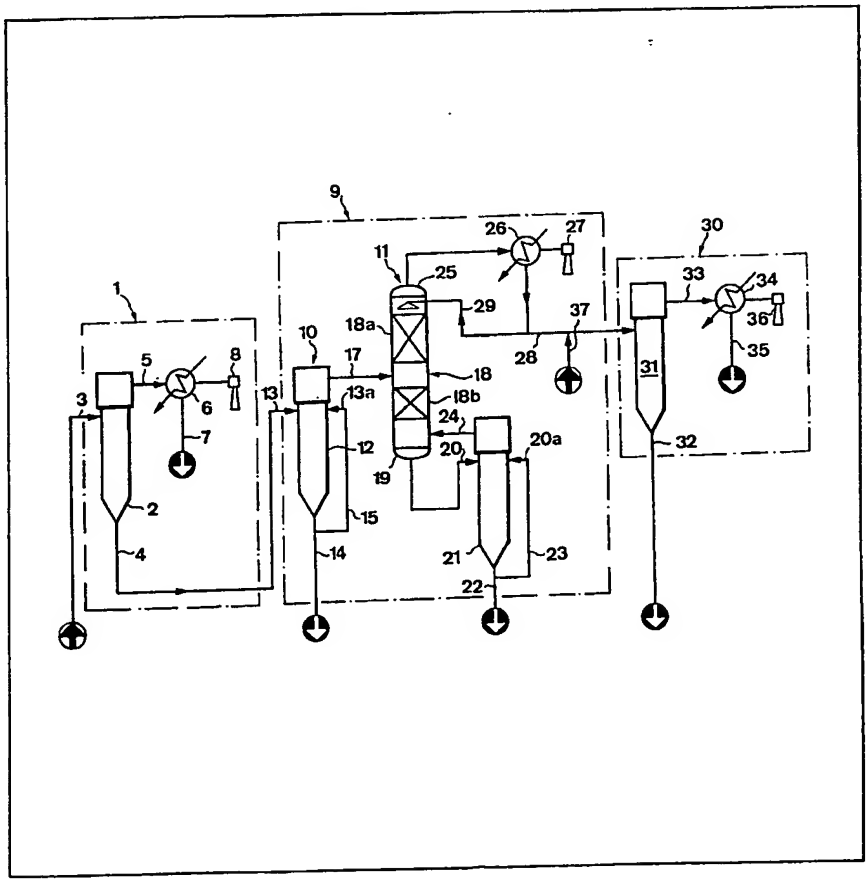
# (54) Method and apparatus for the continuous thermal separation of liquid thermally unstable mixtures

(57) Raw caprolactam, for example, extensively freed in a dewatering stage from solvent is subjected in a separation stage to a distillation and a rectification, without intermediate condensation. The product which is produced by the rectification is then subjected to a thin-film distillation in the presence of an alkaline compound.

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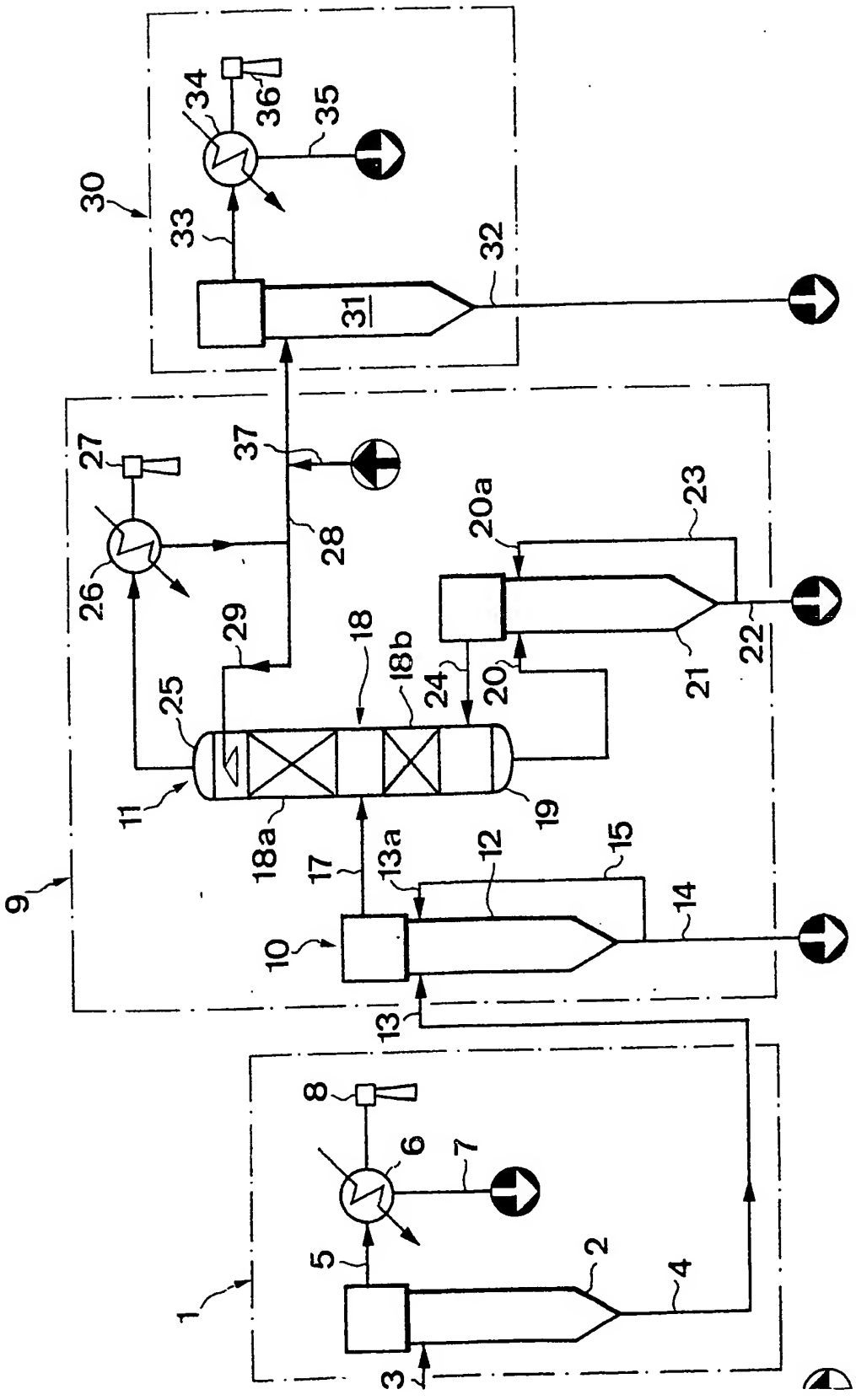
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SPECIFICATION

**Method and apparatus for the continuous thermal separation f liquid thermally unstabl mixtures, especially caprolactam, from impurities predominantly of an acidic nature or neutral derivatives of such impurities**

The present invention relates to a method for the continuous thermal separation of liquid organic product mixtures from impurities of predominantly acidic nature or from neutral derivatives of such impurities, and further to an apparatus for the performance of the aforesaid method. Such methods and apparatuses are particularly suitable for the purification of caprolactam by separating heavy by-products.

It is well known that, for instance, raw or crude caprolactam contains impurities, especially heavy-by-products, which during further processing influence the quality of the final product. In order to obtain caprolactam of a purity suitable for further processing, it is known to chemically separate a portion of the impurities in a pre-purification stage and thereafter to separate the remaining impurities in a final purification stage by physical or thermal action. During the thermal separation in the final purification stage the non-volatile impurities are separated by distillation and the harder to volatize impurities by rectification. This known procedure is however associated with the drawback that it is necessary to provide a multiplicity of individual method stages both for the chemical and for the physical procedures and these are associated with losses. During the chemical pre-purification there are additionally produced salts which deposit at parts of the installation and therefore make it necessary to clean the equipment periodically.

It is an object of the present invention to provide a method of, and apparatus for, the continuous thermal separation of mixtures from impurities, in a manner in which the aforementioned drawbacks and limitations are reduced or eliminated.

According to the present invention, there is provided a method for the continuous thermal separation of a liquid thermally unstable product mixture from impurities of predominantly acidic nature or from neutral derivatives of such impurities, in which the product mixture is subjected in a separation stage to a distillation and a rectification without any intermediate condensation. The product which is produced during the rectification is thereafter subjected, in the presence of an alkali compound, to thin-film distillation.

As mentioned above, the invention is not only concerned with the aforementioned method and the use of the method for producing extremely high purity products, particularly fibre grade caprolactam, but also pertains to an apparatus for carrying out the method. In particular, in a preferred construction of apparatus of this invention there is provided a separation stage for the distillation and rectification of the product mixture without any intermediate condensation. A thin-film distillation unit or device is arranged after the separation stage and serves for the distillation of the product produced during the rectification. Also, an infeed means serves for the introduction of an alkaline compound to the product produced during the rectification.

By virtue of the omission of an intermediate condensation the residence time of the product in the separation stage and equally in the subsequent thin-film distillation stage is extremely short for a given or predetermined temperature, so that the thermo-unstable product experiences a lower temperature.

In the separation stage there are separated for the most part the impurities contained in the starting product, so that the product leaving the separation stage already possesses an appreciable purity. This enables one to obtain by means of the subsequent thin-film distillation, in the presence of an alkaline compound, a final product of high quality and, additionally, of exceptionally high purity. The final product leaving the thin-film distillation unit can therefore be further processed directly. The caprolactam which can be purified by the present invention, is therefore particularly suitable for the production of polyamides, which, for instance, can be processed further to provide man-made or synthetic fibres.

According to a preferred embodiment the product which is produced by distillation carried out in the separation stage is introduced in a vaporous state to the rectification unit or device.

The present invention will now be illustrated, merely by way of example, with reference to the accompanying drawings in which the single Figure illustrates schematically a typical apparatus for carrying out the method of this invention.

Referring to the Figure, the apparatus comprises a dewatering stage 1 for the starting product mixture, for example crude caprolactam. This dewatering stage 1 comprises a thin-film evaporator 2, provided with an inlet, 3, for the raw caprolactam containing, say 20 percent water. An outlet 4 from the thin-film evaporator 2 is connected with a separation unit or stage 9. A condenser 6 is connected with the vapour outlet 5 and by means of condenser outlet or discharge line 7 the water which has been separated can be removed. By means of a vacuum aggregate or device 8 a vacuum can be produced in both the thin-film evaporator 2 and in the condenser 6.

The separator stage 9 (which is downstream of the dewatering stage 1) contains a distillation unit or device 10 and a rectifier or rectification unit or device 11. The distillation unit 10 is constituted by thin-film evaporator 12, whose inlet 13 is connected with the outlet 4 of the thin-film evaporator 2. By means of outlet 14 it is possible to remove the non-distillable, non-volatile impurities which have been separated in the thin-film evaporator 12. The outlet 14 is connected by means of a return flow line 15 with inlet 13a, in order to render possible recirculation or recycling of a portion of the concentrate in the thin-film evaporator 12. Vapour outlet 16 of the thin-film evaporator 12 is connected with the rectification unit 11, i.e. with the infeed line 17 of rectifier column 18. The vapours which are formed in the thin-film evaporator 12 are directly fed

into the rectifier or rectification column 18, whose rectifying section has been generally designated by reference character 18a and whose stripping section by reference character 18b.

Bottom 19 of the rectification column 18 is connected with inlet 20 of a thin-film evaporator 21, from which there can be removed the harder to volatize impurities, by means of its outlet 22. The outlet 22 is connected by means of a return flow line 23 with inlet 20a, so that it is possible to recycle a part of the produced concentrate in the thin-film evaporator 21. The vapour outlet 24 is connected with the bottom 19 of the rectifying or rectification column 18. The vapour for the stripping section 18b of the rectifying column 18 is therefore produced in such thin-film evaporator 21.

Head 25 of the rectifying column 18 is connected to a condensor 26. To produce a vacuum in the separation unit or stage 9 the distillation device or unit 10 is connected by means of the rectification device or unit 11 with a vacuum means 27. In this separation unit or stage 9 there therefore prevails essentially the same vacuum.

The distillate which is produced in condenser 26, e.g. the caprolactam which has extensively been freed of impurities, is withdrawn in a liquid state by means of an out-flow or discharge line 28. A part of the distillate can be recycled by means of a return flow line 29 into the head 25 of the rectifying column 18.

Connected with the separation unit or stage 9 is a thin-film distillation device 30 which contains a thin-film evaporator 31, whose inlet is connected with the outflow or discharge lined 28. Infeed means 37, in the form of an infeed line, opens into this outflow or discharge line 28, and by means of such infeed line 37 it is possible to infeed an alkaline compound, preferably sodium hydroxide, to the product which is infed through the outflow line 28 to the thin-flow evaporator 31.

The residues which are formed in the thin-film evaporator 31 are removed by means of a withdrawal or outfeed line 32. The vapours which are produced in thin-film evaporator 31 are introduced by means of a line 33 to a condenser 34. The distillate produced, in the present case pure caprolactam of extreme purity, can be removed from the thin-film distillation stage 30 by means of a line or conduit 35. This stage 30 furthermore contains a vacuum unit or aggregate 36 for generating a vacuum in the thin-film distillation unit or device 30. By means of vacuum equilibrators 27 and 36 one can ensure that essentially the same vacuum conditions prevail in the separation stage 9 and in the distillation unit 30. Under certain circumstances it would be possible to dispense with one of the vacuum units or aggregates 27 or 36.

The method can be summarized briefly as follows: the starting product mixture (raw caprolactam) freed of the solvent (water) in the evaporator stage 1 is subjected in the separation stage 9 to a distillation and a rectification without intermediate condensation. In the distillation unit or device 10 there are separated the non-distillable residues, i.e. the non-volatile constituents. The vapours are directly infed to the rectifying unit 11 where there are separated-off the harder to volatize constituents. The product which is produced during rectification, and which is extensively freed of impurities, is subsequently subjected to a thin-film distillation in the presence of an alkaline compound. The thus produced end or final product (pure caprolactam) has an extremely high degree of purity.

Since, as already mentioned, the impurities contained in the starting product mixture can be extensively separated-out in the separation or separator stage 9, it is possible, by virtue of the subsequent thin-film distillation, which is important for success, in the presence of an alkaline compound to obtain a high quality end product of extremely great degree of purity, which can be used directly for the production of polyamides. Since the distillation and the rectification is accomplished in the separation stage 9 without any intermediate condensation, the thermally unstable product has a short residence time in separation stage 9. The same holds true for the thin-film distillation unit 30 where the product is subjected to a protective distillation with a short residence time. In the thin-film evaporator 31 an evaporation or vaporization occurs without any reflux, where the product is subjected to the boiling temperature for the briefest amount of time which is absolutely necessary.

The equipment needed to obtain the pure caprolactam according to the invention is relatively simple in construction and design and only requires a few individual stages.

With the method of this invention it is possible to extensively eliminate, during the purification of caprolactam, both the volatile bases and the amides of hexahydrobenzoic acids. The caprolactam removed from the rectification unit 11 generally contains only approximately 0.001 percent of such amides, whereas the starting content of such amides at the inlet 13 to the separator or separation stage 9 may be 0.1 percent.

The separation action of the separation stage 9 is illustrated in the following table based upon a pilot test:

| Position in Schematic Drawing | Inlet 13 | Outlet 14 | Outlet 22 | Outflow Line 28 |
|---|---|---|---|---|
| Designation | Feed | Bottom 1 | Bottom 2 | Distillate |
| Quantity in Kg/h | 45 | 2.6 | 3 | 39.4 |
| Impurity (Amide) meq (milli-equivalent)/Kg | 17.8 | 64.2 | 210 | 0.16 |

The permanganate number or coefficient, characteristic of the degree of purity, at the outlet 28 of the rectification unit or device 11 amounted to somewhat more than 2000 (using the determination method of the Italian Firm SNIA VISCOSA Societa Nazionale Industria Applicazioni Viscosa S.p.A., of Milan, Italy. This permanganate number is not sufficiently high in order to obtain caprolactam of "fibre grade", i.e. of the highest degree of purity. Notwithstanding the extremely good purification action of the separation stage or unit 9 the product which is produced during rectification therefore is not yet suitable for direct fabrication of polyamides. During the subsequent thin-film distillation in the distillation unit 30, accomplished in the presence of an alkaline compound, this permanganate number rises to a value which is above 8000. This means that at the outlet 35 of the thin-film distillation unit 30 there appears pure caprolactam of extremely great purity ("fibre grade").

Although for the evaporation in stage 1 and the distillation in stage 9 thin-film evaporators are particularly suitable, it is also conceivable to employ, instead of the thin-film evaporators 2 and 12, different types of evaporators. It is equally possible to use, instead of the thin-film evaporator 21 of the rectifying unit 11, a different type of evaporator. As the rectifying column 18 there can also be employed all suitable apparatuses which are appropriate for vacuum rectification.

Although the detailed embodiment has been described for the purification of caprolactam, the method and apparatus can also be employed in an appropriate fashion for the continuous thermal separation of other liquid thermally unstable product mixtures from impurities of predominantly acidic nature or neutral derivatives of such impurities.

CLAIMS

1. A method for the continuous thermal separation of a liquid thermally unstable mixture from impurities predominantly of acidic nature or from neutral derivatives of such impurities, which comprises:
distilling and rectifying, without intermediate condensation, the mixture in a separation stage and thereafter exposing the product obtained during recification to a thin-film distillation in the presence of an alkaline compound.
2. A method according to claim 1 in which the mixture is a liquid mixture containing crude caprolactam.
3. A method according to claim 1 or 2 in which the alkaline compound is sodium hydroxide.
4. A method according to any one of claims 1 to 3 in which the distillation and rectification are carried out under vacuum conditions.
5. A method according to any one of the preceding claims in which the thin-film distillation is carried out under vacuum conditions.
6. A method according to any one of the preceding claims in which the mixture is a liquid mixture containing a solvent and prior to distillation in the separation stage the liquid mixture is extensively freed from the solvent.
7. A method according to any one of the preceding claims which comprises feeding in a vaporous state the product produced by distillation to a rectifying unit.
8. A method according to any one of the preceding claims in which the distillation is carried out in a thin-film evaporator.
9. A method according to claim 8 which comprises recycling part of the product in the thin-film evaporator.
10. A method according to claim 1 substantially as hereinbefore described.
11. A mixture freed from impurities by a method as claimed in any one of the preceding claims.
12. Caprolactam whenever produced by a method as claimed in any one of claims 1 to 10.
13. An apparatus suitable for the continuous thermal separation of a liquid thermally unstable mixture from impurities of predominantly acidic nature or from neutral derivatives of such impurities, which comprises: a separation stage for the distillation and rectification, without intermediate condensation, of the mixture; a thin-film distillation unit connected to the distillate outlet from the rectification stage; and means

for introducing an alkaline compound to the product produced during rectification.

14. An apparatus according to claim 13 wherein: said separation stage contains a distillation unit and a rectification unit, said distillation unit having an outlet for vaporous products which directly connected to an inlet of said rectification unit.

15. An apparatus according to claim 13 or 14 in which said distillation unit comprises a thin-film evaporator.

16. An apparatus according to any one of claims 13 to 15 which also includes vacuum means connected to said rectification unit and said distillation unit.

17. An apparatus according to any one of claims 13 to 16 which also includes an evaporator connected upstream of said distillation unit of the separation stage for at least partially removing solvent from the starting mixture.

18. An apparatus according to claim 17 wherein: said evaporator is a thin-film evaporator.

19. An apparatus according to claim 13 substantially as described with reference to the Figure of the accompanying drawing.

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